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Thin Film Techniques for Solid State Ionic Devices

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Abstract

The perovskite of type LaCrO_3 has been previously shown to be an excellent sense electrode for a new type of mixed potential sensor. Techniques for the growth and patterning of thin film electrodes with stable morphology and reproducible stoichiometry grown on yttria-stabilized zirconia solid electrolyte have therefore become extremely desirable. In this work, thin films of LaCrO_3 and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ were prepared using RF magnetron sputtering, electron beam evaporation and pulsed laser deposition. Direct growth of the perovskite from oxide targets were usually accompanied by second phases with Cr in valance states higher than 3^+ . Films prepared by an intermediate fluoride process via off-axis RF magnetron sputtering process produced the highest quality films but the deposition rate was typically low at approximately $1500\text{\AA}/\text{hr}$. Stoichiometric films were prepared using an electron beam/thermal evaporation dual source method but not reproducibly. Single-phase lanthanum chromite films could not be prepared using PLD and a fluoride precursor.

Introduction

The role of high temperature, solid-state electrochemical sensors may become more pronounced in the near future. Calls for improved combustion

efficiency in power plants, NO_x emissions monitoring of exhaust gases from natural gas-fired stationary reciprocating engines and from small gas-fired appliances, improved hydrocarbon/carbon monoxide sensors for automobile On-Board Diagnostic systems, and in-flue gas CO sensors for appliance safety are strong motivations to research and develop new types of electrochemical sensors. All of the aforementioned applications will require a robust, long-lived sensor technology capable of surviving harsh environments.

The most ubiquitous high-temperature electrochemical sensor in use today is the lambda sensor used in the combustion control system and in the OBD systems for automobiles and light trucks. Presently, most lambda sensors are made from a small thimble-shaped tube of yttria-stabilized zirconium (YSZ) oxide solid electrolyte with inner and outer surfaces covered with Pt electrodes. The success of this sensor in the automotive applications is due mostly to the robust chemical and thermodynamic stability of the low cost YSZ solid electrolyte. Unlike YSZ, Pt is expensive but only a small amount is required for the electrodes. Much of the success of this sensor can also be attributed to operating principle of the device: this sensor is a sensor of Type 1 where by the analyte to be sensed – O₂ – is the species transported through the solid electrolyte. (1)

In recent years, we have used the zirconia-based lambda sensor - and its intrinsic advantages - as a starting point for research to develop new electrochemical sensors. (2-5) The replacement of the Pt working electrode with advanced electronic, refractory transition metal oxides has permitted the development of sensors for applications where, up to now, either no sensor

technology existed or in applications where sensors to sense a particular gas species exist but are either inadequate to fulfill the sensing requirements or are simply too expensive for intended widespread use.

One type of electrochemical sensor known to the solid-state sensor community for some time is the mixed-potential sensor. (6-9) Because of the significant amount of research conducted by many researchers over the past twenty-five years, a detailed description of the mixed potential phenomena will not be presented here, rather, only a summary. When a YSZ electrolyte-based oxygen sensor is exposed to carbon monoxide (CO), hydrocarbons (HCs), or nitrogen oxides (NO_x) in the presence of oxygen at temperatures less than 800°C, a non-nernstian potential develops at the electrodes (8, 9). This non-equilibrium potential is controlled by the kinetics of the various oxidation and reduction reactions and is known as the mixed-potential. The mixed potential response of various metal and metal-oxide electrodes have been studied in the past and several sensor designs have been proposed to sense CO (10, 11), HCs (12, 13), and NO_x (14, 15).

Two factors are critical in determining the response of mixed potential sensors. [16-18] First is the oxygen reduction kinetics at the electrode/electrolyte interface; the second is the amount of heterogeneous catalysis of the gas species before reaching that interface. For sensors based on a Pt counter electrode, the sensor response was found to improve with a decrease in the oxygen reduction kinetics at the sensing electrode (16, 17). Moreover, it has been reported that greater heterogeneous catalysis on the sensor body results in

a decreased concentration of analyte species at the electrode/electrolyte interface and therefore a lower mixed potential (17, 19).

Therefore, tailoring the response of a mixed potential sensor for a desired gas sensing application becomes a delicate balance between multiple electrochemical reactions, the electronic properties of the electrode, and the catalytic and electro catalytic properties of the electrode material and solid electrolyte at the gas/electrode/solid electrolyte interface (triple phase boundary, or TPB).

We have recently reported new mixed potential sensors that are reproducible and stable over time by creating an electrode/electrolyte interface that does not change either morphologically or by chemical reaction with the surrounding environment (20-22). This work demonstrated that the aging and irreproducible sensor response characteristic to mixed potential sensors might be overcome. This was accomplished by using a machined slug of stable, refractory ceramic, metal oxide such as $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ embedded into YSZ solid electrolyte. One face of the ceramic slug is exposed to the atmosphere. The perimeter of the slug is in contact with the YSZ. The counter electrode consisted of a simple Pt wire also embedded into the YSZ. The whole device is co-fired at elevated temperature. Furthermore, multiple sensors were fabricated that yielded the same response characteristics – e.g. voltage level, response time, etc.

Work continues to advance thin film mixed potential sensors by applying analogous design concepts from bulk sensor development. However, advancements in engineering stable and reproducible thin film devices have

been slower to develop. The reason for this is that the properties of thin films prepared at reduced temperatures on substrates composed of different materials can differ substantially from the properties of the same materials processed single phase at high temperatures and then co-fired to produce a working sensor.

A change in the materials properties of a mixed potential electrode at elevated temperature is an example of the very reason why mixed potential sensors based on zirconium oxide have not been commercialized despite over 20 years of research. The thin Au films used as a working electrode are not morphologically stable at elevated operating temperatures (16). Moreover, we have shown that even the metallization used to make electronic contact with thin film metal oxide electrodes that we have substituted for the Au working electrode can affect the mixed potential response and consequently lead to sensors that are both irreproducible and unstable over time (23, 24).

As with the bulk sensors, engineering reproducible mixed potential thin film sensors will be governed by the stability of the electrode/solid electrolyte interface together with the thermodynamic and chemical stability of the electrode material itself. In previous work we have shown that as with the bulk, ceramic sensors, thin film sensors with ceramic working electrodes with a well defined and reproducible electrode/solid electrolyte interface show stability and reproducibility. Devices based on thin film electrodes and electrolytes are very desirable for many reasons. Planar designs utilizing tape-casted, multilayer green bodies permits large numbers of devices to be produced at a low cost. An example of this is the planar lambda sensors for automotive applications. Planar

sensors readily permit the incorporation of heaters and their low mass provide for rapid heat up and thermal stabilization.

Another motivation to pursue the development of thin film mixed potential sensors is that combining mixed potential sensor technology with micro-machined silicon heater technology may pave the way for truly versatile and capable gas sensors. Mixed potential sensors can have a large temperature coefficient of sensitivity (6,7,25). In fact, issues with cross sensitivity may easily be mitigated if the temperature coefficients exhibited by the various metal oxides studied to date are exploited. E.g. an array of microelectrodes made from different ceramics each operating at an optimized temperatures on a common substrate may provide freedom to tailor mixed potential sensors for specialized applications. A substantial amount of research will be necessary before the aforementioned scenario can be realized however. Understanding the factors that affect film growth (the coefficient of thermal expansion, materials compatibility during nucleation and growth, etc.), electronic and ionic properties as well as catalytic and electro-catalytic properties of the electrode ceramics and actually controlling these properties through intelligent deposition and growth will be required.

Los Alamos has been engaged in sensor research and development over the past decade. We have explored new sensors for numerous applications including amperometric lean burn O_2 sensors (3,4) for automotive applications, O_2 sensors for industrial boiler control in high sulfur environments (26), HC mixed potential sensors for catalytic On-Board Diagnostics (OBD-II) (23, 24), and now mixed

potential NO_x sensors for emissions monitoring for stationary power. Regardless of the nature of the device and application -amperometric, potentiometric, or kinetic- these devices require high quality thin films of either mixed conductors and/or solid electrolytes – advanced materials that permit the development and testing of sensors for unique and demanding applications. Techniques to grow ceramic thin films are an important and critical component of our to on-going sensor program at Los Alamos. In this work, we will present our recent progress in ceramic thin film research as well some notable milestones from the recent past.

Experimental

In this work, fluoride or oxide thin films were prepared using multiple techniques. The experimental method used for each deposition method will be individually outlined in detail below. The substrates used and, their preparation were common to each method. Cera-Flex™ brand yttria-stabilized zirconia, (YSZ) obtained from Marketch International in 0.5x100x100 mm sheets, was cut into 1 cm² substrate wafers using a diamond saw. The substrates were ultrasonically cleaned in isopropanol or acetone and then dried and fired in air at 1100°C for several hours. The YSZ wafers were mounted onto a Ni faceplate that was subsequently placed into contact of a boron nitride heater specifically designed for vacuum operation. The substrate was typically held to the Ni faceplate by an alumina mask held by a metal clip or glued (silver/water-based epoxy from AREMCO) to the faceplate using a silver-based epoxy. The substrate temperature was monitored using a thermocouple embedded within the

faceplate. Typically, a masked piece of polished sapphire was mounted next to the substrate. The step height created on this witness sample was then used to measure the film thickness produced in the run using a Dektak profilometer.

Fluoride RF Magnetron Sputtering

LaF_3 , XF_2 ($\text{X}=\text{Sr}, \text{Mg}$) and chromium metal (average particle size $< 10 \mu\text{m}$) were obtained from Acros and Alfa Aesar respectively. A stoichiometric amount to yield a cation ratio of $\text{La}:\text{X}:\text{Cr} = 0.8:0.2:1$ or $1:0.2:0.8$ were weighed and placed into a polypropylene ball mill container along with isopropyl alcohol and zirconia grinding media. The mixture was ball-milled for 6 hours. The slurry was collected and dried at 35°C . The powder was then placed into a 2" diameter steel die and pressed at 400 pounds total pressure for 5 min. The pellet was removed from the die, placed onto an alumina support disk and placed in a high temperature tube furnace. The target was heated at $2^\circ\text{C}/\text{min}$ to 1100°C , held for 500 min, and cooled to room temperature at $2^\circ\text{C}/\text{min}$ in an atmosphere of dry Ar. The sintered target was removed and mounted in a 2" diameter copper RF magnetron sputter cup using Ag epoxy (SPI). The completed sputter target was transferred to a RF magnetron sputter system.

A CereFlex™ brand YSZ substrate was mounted to Ni faceplate of the boron nitride vacuum heater assembly. A masked sapphire witness was affixed along side the substrate and was used to subsequently determine film thickness using a DEKTAK profilometer. The sputter deposition was carried out at ambient sputter temperature (if sensor electrodes were patterned using a tape/lift-off

process – Scotch brand Kapton industrial tape) or at 400°C (if electrodes were patterned using an alumina mask). The films were grown in a UHP Ar atmosphere at 40 μm pressure and at a power setting of 125W.

Fluoride Electron Beam Evaporation

LaF_3 , SrF_2 and chromium metal (average particle size < 10 μm) were again obtained from Acros and Alfa Aesar. Film preparation using a dual source approach was used in this work. Two fluoride targets were prepared. The first target was single-phase LaF_3 . A pellet was formed in a 0.75 in. die using a uniaxial press. No sintering was required. The second fluoride target was prepared by measuring a stoichiometric amount of powder to yield a cation ratio of $\text{La}:\text{Sr} = 0.8:0.2$. The powders were weighed and placed into a polypropylene ball mill container along with isopropyl alcohol and zirconia grinding media. The mixture was ball-milled for 6 hours. The slurry was collected and dried under low heat. Pellets of this two-phase mixture were prepared by placing the powder into a 0.75 in. die and applying uniaxial pressure as before. No sintering was required. Depending on the desired film composition of the deposition, one of the pellets was placed into a thermal evaporation hearth in the electron beam deposition system. The pellet was lightly broken into smaller chunks and arranged to evenly fill the evaporation boat. The electron beam hearth was loaded with small nuggets of Cr metal. A series of calibration runs were first required in order to find deposition rates that produced films with the desired stoichiometric ratio of $\text{LaF}_3:\text{Cr}$ or $\text{LaF}_3:\text{SrF}_2:\text{Cr}$. Substrate temperature was maintained at various

temperatures depending on the deposition. The typical substrate temperature was held between 200 and 400°C through out the run. The heater faceplate (and affixed substrate) was positioned on-axis for the electron beam depositions, approximately 6 inches away from the sources and centrally located between the two sources. A pair of quartz crystal rate monitors each located next to its respective source were used to control the material deposition rate.

Fluoride Pulsed Laser Deposition

For films prepared using PLD, $\text{LaF}_3/\text{SrF}_2/\text{Cr}$ target pellets were prepared in the same fashion as for RF sputtering. The size of the target was approximately 0.75" dia. x 0.5" thick. The target was mounted into a high vacuum chamber of a PLD system. A xxxxx laser xxxx xxxx xxxx . Aluminum oxide cut into 1 cm² wafers glued to a Ni heater faceplate served as a substrate for film growth.

Post Fluoride Film Growth Processing

The $\text{LaF}_3/\text{SrF}_2/\text{Cr}$ films were processed using an identical procedure regardless of the technique in which they were prepared. The fluoride/chromium films were removed from the deposition system and transferred to a tube furnace. A switching system was set-up to switch from neat Ar to humidified Ar (gas bubbled through water at 25°C) using a three-way valve. The films were heated at 10°C/min to 800°C in dry Ar. At 800°C the gas was switched to humidified Ar and the sample was annealed at 800°C for 15 minutes. The thin

film sample was heated to 1000°C in dry Ar and held for several hours to make sure the film was completely crystallized.

Direct Oxide RF Magnetron Sputtering

Substrates were placed into an ultra-high vacuum sputter system using the same heater as was used in the fluoride depositions. Depositions were made using 90° off-axis radio frequency (RF) magnetron sputtering technique from a single 2-in. powder target. The LaMnO_3 (LMO) and $\text{Y}_{0.16}\text{Tb}_{0.30}\text{Zr}_{0.54}\text{O}_{2-\delta}$ (TbYSZ) target powders were made using standard solid-state reaction techniques. Following x-ray diffraction (XRD) characterization, the powders were packed into 2-in. diameter copper sputter cups to a depth of 0.125" and mounted into the sputter gun in the same manner as a hard target. The sputter conditions for both LMO and TbYSZ film depositions were 90° off axis, a 700°C – 800°C heater faceplate temperature, a chamber pressure of 40 mTorr of Ar and a RF power of 100 – 125 watts.

Following deposition and subsequent reaction/annealing (if required), the films were characterized using a variety of methods. A Siemens D5000 x-ray diffractometer (XRD) using CuK_α radiation and a Ge single crystal, incident beam monochromator was used to determine the film crystal structure, phase purity and lattice parameters. A second Siemens D5000 was also may have been employed – this instrument differed from the previous in that does not have an incident beam monochromator to eliminate $\text{CuK}_{\alpha 2}$. The analysis of the XRD data

was carried out using the SHADOW™ full profile refinement package written by Materials Data Corporation.

Film composition was measured using a Spectrace QuanX Energy Dispersive X-ray Fluorescence Analyzer (XRF) equipped with a LN₂-cooled Si(Li) detector. The weight-percentages of LaF₃, La₂O₃, SrF₂, SrO, and Cr/Cr₂O₃ were calculated using a fundamental parameter method included in the QuanX™ analysis software. An advantage of the fundamental parameter method over older empirical standards method is the elimination of the many calibration standards typically required to accurately model a wide range of film stoichiometry. The models were tested against bulk and thin film La-Sr-Cr standards with known composition. The fundamental parameter method only requires a single calibration standard per element. A Perkin Elmer TGA 7 was used for thermogravimetric measurements. Film thicknesses were determined using a DEKTAK profilometer. A Phillips XL-20 digital scanning electron microscope provided images of film morphology.

Results and Discussion

Figure 1 shows the XRD traces of two films prepared via on-axis RF magnetron sputtering from a compacted powder LaCrO₃ oxide target prepared in house. On-axis sputtering was chosen to maximize film growth rate for desired thicknesses on the order of 1 to 5 μm. The film shown in Figure 1a was grown for 24 hours on fully-stabilized YSZ at a substrate temperature of 650°C. The background atmosphere was 40 mTorr of 60%O₂/40%Ar mixture. The principal impurity phase noted in the figure is La₂CrO₆. Full profile fitting yielded lattice

parameters of $a=5.5307(0.0004)\text{\AA}$, $b=7.8448(0.0005)\text{\AA}$, and $c=5.651(0.003)\text{\AA}$ (error in parentheses) and is close to JCPDF values (card# 33-0701). The deposition rate was 1983\AA/hr . Figure 1b shows the XRD trace of a second film prepared at 650°C in pure Ar for 5 hrs. Full profile refinement gave lattice parameters of $a=5.552(0.001)\text{\AA}$, $b=7.879(0.004)\text{\AA}$, and $c=5.650(0.02)\text{\AA}$. This film was thinner, given the reduced sputter time; however, the rate was higher at 2324\AA/hr most likely due to reduce back sputtering from the oxygen ions. The some of the principal impurity peaks are indicated and may be due to the presence of La_2O_3 and Cr_2O_5 . As can be seen in Figure 1, the films that were prepared from an oxide target typically contained additional phases although the primary phase present was LaCrO_3 . In $60\%\text{O}_2$, the indicated second phase was easily identified as La_2CrO_6 . In this lanthanum chromite phase, Cr is in the Cr^{+6} and indicates that the conditions for growth of Cr^{+3} phases were less than ideal. Even in pure Ar, a higher chromium valance state was produced most likely due to elevated oxygen partial pressures due to oxygen ions in the plasma from the oxide target. Higher substrate temperatures in Ar may have reduced the tendency to form Cr valences greater than +3 but high deposition temperatures would complicate sensor fabrication.

For mixed potential sensor applications, the presence of additional phases in the electrode is undesirable. The second phases will affect the electronic and ionic conductivities of the thin film and may produce unpredictable changes in catalytic properties on the surface of the metal oxide electrode. Since the motivation for this research is the development of stable mixed potential sensors

with reproducible response characteristics - utilizing the structural and thermodynamic stability of advance metal oxide electrodes – electrodes must be produced with completely reproducible properties. The growth of stoichiometric doped and undoped La-Cr-O perovskite films from other methods was then explored.

The preparation of oxide thin films from a multiphase mixture of metals and fluorides has been reported in the literature for the preparation of high quality, stoichiometric YBCO high- T_c superconductors (27). Stoichiometric mixtures of LaF_3 , SrF_2 , and Cr were prepared and studied using thermogravimetric analysis. Figure 2 is a TG analysis of a three phase mixture of $\text{LaF}_3/\text{SrF}_2/\text{Cr}$ in the presence of a dry Ar atmosphere ($P_{\text{H}_2\text{O}} < 50$ ppb) and Ar humidified by bubbling the Ar through water at a temperature of 50°C . The samples were both heated at $10^\circ\text{C}/\text{min}$ to 1000°C . Figure 2 shows that the 3 phase mixture is stable up to 1000°C . However, if water is introduced into the system above 800°C , reaction concomitant with a weight loss is clearly evident. XRD analysis of the humidified sample post-TGA shows the presence of the $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ perovskite however, the perovskite could never obtained in single phase despite prolonged anneals at 1000°C . The weight loss in Figure 2 is the decomposition of the La and Sr fluorides into oxides and the oxidation of the Cr metal. HF is subsequently produced and is flushed out of the system. The normal reaction temperatures to produce single phase $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ from oxide precursors is well in excess of 1000°C . Therefore, once the decomposition of the fluorides concluded, the

kinetics were sufficiently slow that subsequent reaction to form the perovskite ceased.

The stability of the three-phase mixture in the absence of water was confirmed while making a fluoride target for RF sputtering. Figure 3 is the XRD trace of 2 inch diameter (by 0.125 inch thick) target of $\text{LaF}_3\text{:SrF}_2\text{:Cr} = 0.8\text{:}0.2\text{:}1$ made for a standard 2 in. RF magnetron sputtering gun. The target was pressed in an uniaxial die and sintered at 1100°C in dry Ar for 2 hrs. The three phases are indicated; no reaction peaks could be found.

Figure 4 shows the XRD trace of a thin film sputtered off-axis from the three phase fluoride target at 25 and 400°C respectively as deposited (28). On axis deposition for faster deposition rates was not possible because doing so caused significant reactive sputtering that etched the substrate at rates as high as several thousand angstroms per hour. The thicknesses of the composite films shown in Figure 4 were 4000 and 6500Å respectively. The typical sputter rate for off-axis deposition was on the order of 1500Å/hr. The composite film grown at 400°C showed evidence of crystallinity. However, after annealing in Ar/ H_2O at 1000°C , a single phase $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ film was produced (28) For sensor applications, a thick film on the order several microns is desirable. Figure 5 shows the XRD trace of a thick (1.2 μm) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ film made by an extended sputter deposition (8 hr), post optimization with a fresh target and subsequent anneal in Ar/ H_2O . The film is single phase $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$. The lattice parameters from full profile refinement are: $\mathbf{a}=5.4523(0.0007)\text{\AA}$, $\mathbf{b}=5.4523(0.0002)\text{\AA}$, and $\mathbf{c}=13.443(0.002)\text{\AA}$. The intimate mixing of the fluorides and Cr metal from the

vapor state is clearly sufficient to produce a single-phase perovskite well below the normal synthesis temperatures for La-Sr-Cr-O.

The thick film obtained by a lengthy sputter run shown in Figure 5 showed that high quality, single-phase La-Sr-Cr-O electrodes could be prepared via sputtering. However, the rate was still considered to be slow for routine sensor electrode fabrication. Faster rates would be desirable. Electron beam evaporation is known for producing high quality films at rates generally considered much higher than for RF sputtering. Our goal was to learn how to optimize the electron beam process to obtain rates on the order of several thousand angstroms per minute compared to approximately one thousand angstroms per hour obtained via off axis sputtering.

Our initial work showed that stoichiometric fluoride/chromium metal films could not be prepared from a single $\text{LaF}_3/\text{SrF}_2/\text{Cr}$ source. Dual electron beam evaporation also proved to be inadequate due to the difference in vapor pressure of the target constituents. However, we succeeded in preparing stoichiometric films by a simultaneous, dual-source method using a thermal evaporation source for the fluoride target and an electron beam source for the Cr metal. The first successful films prepared were undoped LaCrO_3 . Figure 6 is the XRD trace for a $1.5\text{ }\mu\text{m}$ thick film grown on fully stabilized YSZ. The deposition time for this film was 15 min or $60000\text{ }\text{\AA}/\text{hr}$ directly comparing to the time scale used for sputtering. The substrate temperature was 400°C . This stoichiometric film was prepared at source rates of $5\text{ }\text{\AA}/\text{sec}$ and $10\text{ }\text{\AA}/\text{sec}$ for the thermal (LaF_3) and electron beam (Cr) sources respectively. The total thicknesses measured using the quartz rate

monitors were 8973Å and 4513Å respectively. The recorded pressure was 10^{-6} atm. A full profile fitting of the XRD data yielded lattice parameters (orthorhombic unit cell) of $a=5.513(0.002)\text{Å}$, $b=5.478(0.003)\text{Å}$, and $c=7.772(0.002)\text{Å}$.

Although these data show that single phase LaCrO_3 can be prepared using electron beam and thermal evaporation, it was found to be quite difficult to do consistently. The rates given above had to be individually determined for each batch of source material that was prepared. Typically, several depositions were required along with several attempts to prepare a single stoichiometric film. The situation became more difficult when Sr-doped LaCrO_3 films were prepared.

Figure 7 shows the XRD of a strontium-doped lanthanum chromite film prepared on a YSZ substrate using the dual source approach. To prepare this film, a stoichiometric mixture ($\text{La}:\text{Sr} = 0.8:0.2$) of La and Sr fluoride was placed into the thermal hearth. As before, chunks of chromium metal were placed into the electron beam hearth. The evaporation rates were 14.5Å/sec for the $\text{LaF}_3/\text{SrF}_2$ and 2.7Å/sec for the Cr. The run lasted 3.3 min. The thickness of the film was $0.4\text{ }\mu\text{m}$ for a total deposition rate of close to 72000Å/hr . The substrate reflections for the fully stabilized YSZ are marked. The lattice parameters for this film were found using full profile fitting: $a=5.473(0.016)\text{Å}$, $b=5.473(0.004)\text{Å}$ and $c=13.45(0.02)\text{Å}$ (hexagonal unit cell). These values compare well with literature value (PDF#32-1240).

Although both undoped and Sr-substituted lanthanum chromite films were prepared using this evaporation approach, single-phase films – as determined by XRD – were difficult to prepare. Many calibration depositions were required

before a single-phase film could be prepared. After calibration, typically several runs were required before a single-phase film could be made. New calibration runs were required if deposition parameters such as substrate temperature, thickness, source material, or pressure were changed in between or during the runs. Because of these difficulties, pulsed laser deposition was next examined.

Thin film $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ growth from PLD is not new. [29] However, an oxide target was used in this work. In this work, we examined whether the fluoride route would work. PLD Several depositions were performed using the same conditions used for sputtering: 400°C , Ar at 10^{-6} atm of pressure. The target material was a $\text{LaF}_3/\text{SrF}_2/\text{Cr} = 0.8:0.2:1$ sintered pellet prepared in identical fashion to the target prepared for RF sputtering. Figure 8 is the XRD trace of a $1.0\text{ }\mu\text{m}$ thick film grown on polycrystalline Al_2O_3 after reaction in humidified Ar at 1000°C . The reflections for the Al_2O_3 and $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ thin film. However, also labeled are a significant number of reflections due to phases other than the lanthanum chromite. Comparison of the integrated intensities of the principal reflections shows that the lanthanum chromite phase is actually the minority phase produced during the deposition and post-anneal.

XRF was performed on the target material made this deposition. The analysis showed a calculated composition of $\text{LaF}_3 = 66.5 \pm 0.5\text{ wt.}\%$, $\text{SrF}_2 = 11.8 \pm 0.1\text{ wt.}\%$ and $\text{Cr} = 21.7 \pm 0.2\text{ wt.}\%$. This compared well with the theoretical starting material composition of $\text{LaF}_3 = 67.0\text{ wt.}\%$, $\text{SrF}_2 = 10.7\text{ wt.}\%$, and $\text{Cr} = 22.3\text{ wt.}\%$. Analysis of the films post fluoride decomposition showed that the film was La_2O_3 rich and Cr deficient. Since the film was reacted, a different fundamental parameters

model had to be used based on oxides. For the film in Figure 8, the calculated weight percentages were $\text{La}_2\text{O}_3 = 76.9 \pm 0.6$ wt.%, $\text{SrO} = 12.0 \pm 0.5$ wt.%, and $\text{Cr}_2\text{O}_3 = 11.1 \pm 0.2$ wt.%. The theoretical numbers for bulk $\text{La}_{0.8}\text{Sr}_{0.2}\text{CrO}_3$ are 57.4, 9.1, and 33.5 wt. % for La_2O_3 , SrO , and Cr_2O_3 respectively. Studying the XRD trace of the pre-annealed film grown on the sapphire witness may elucidate a possible cause for the non-stoichiometry. This XRD trace is shown in Figure 9. Unlike composite fluoride films derived from the previous methods, this trace shows significant crystallinity of the pre-oxide phases compared to film obtained by sputtering. Figure 9 shows reflections that can be easily assigned to Cr and SrF_2 although there are no reflections that can be assigned uniquely to fluorocite (LaF_3) despite the excess La_2O_3 found in the reacted film.

Although we have not confirmed this, we believe that the target was too inhomogeneous for the nature of the pulsed laser deposition. The in homogeneity of the target lead to a precursor film that was too inhomogeneous to react to a single-phase oxide film. Future work will investigate PLD deposition from targets made smaller particle sizes and more intimately mixed components.

Conclusions

Future work for sensor development will focus on the growth and characterization of stable metal oxide films for mixed potential sensors.

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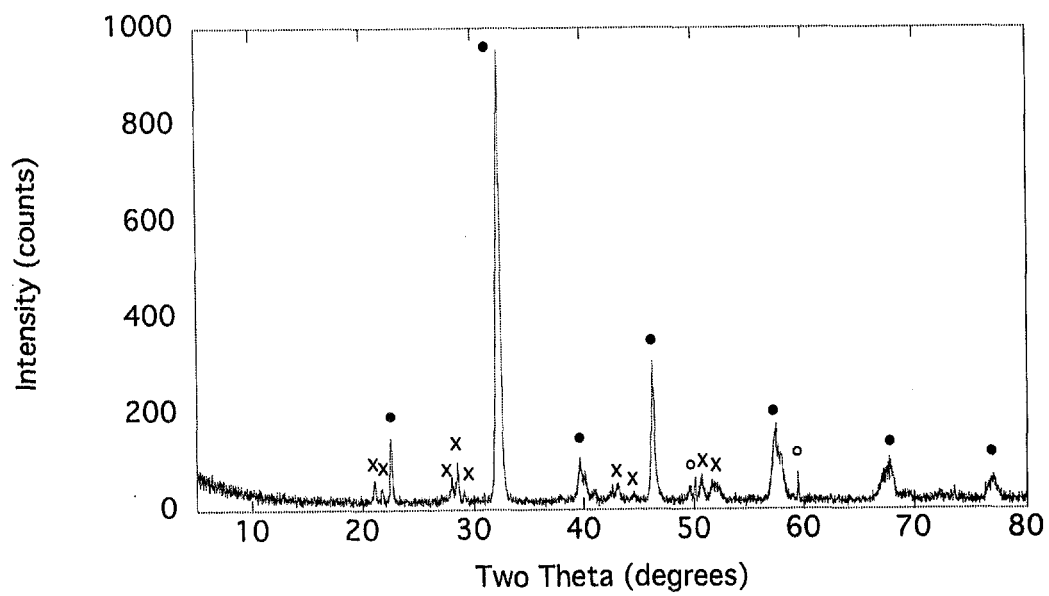


Fig 1a

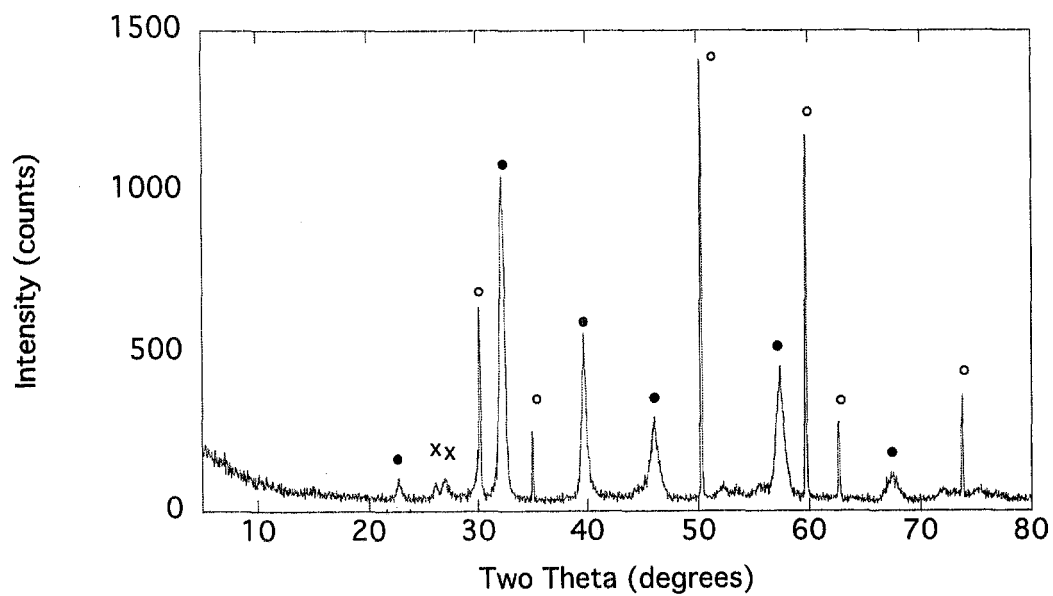


Fig 1b

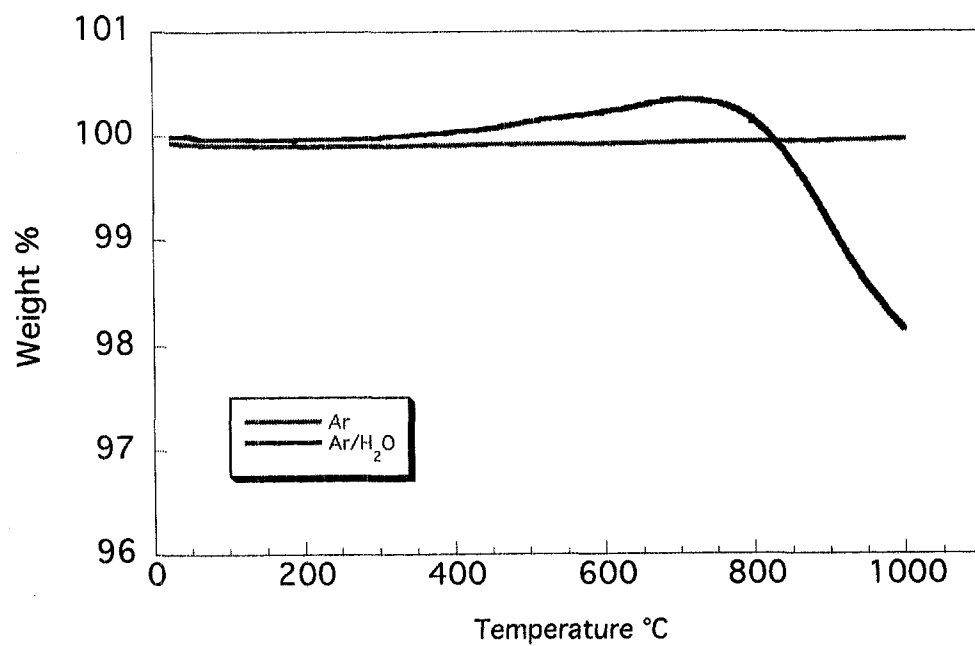


Fig 2

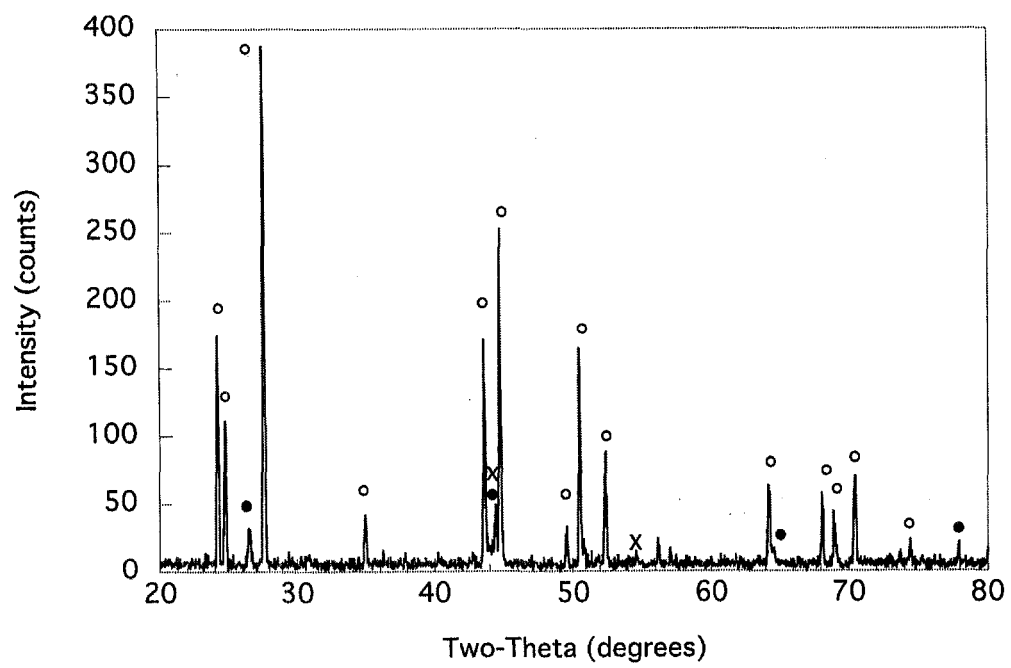


Fig 3

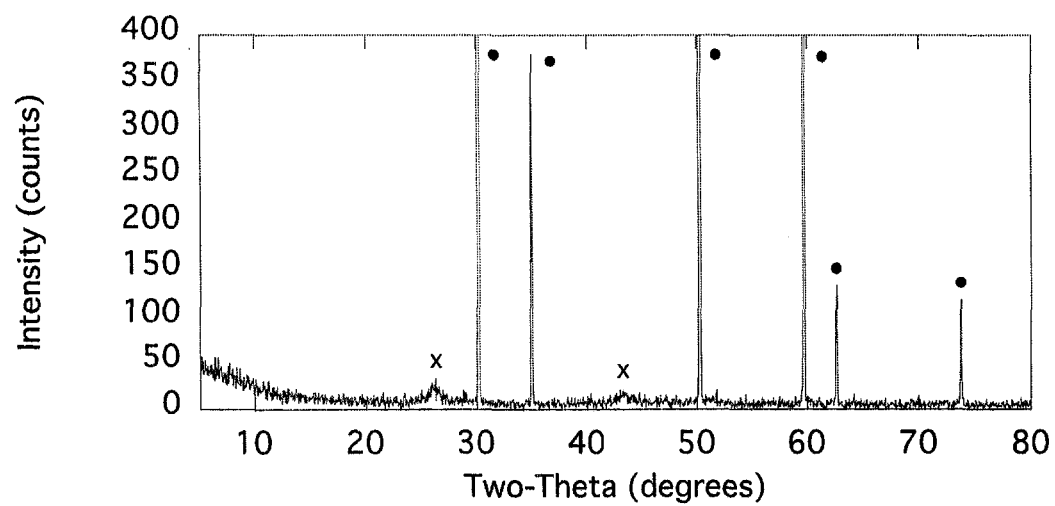


Fig 4a

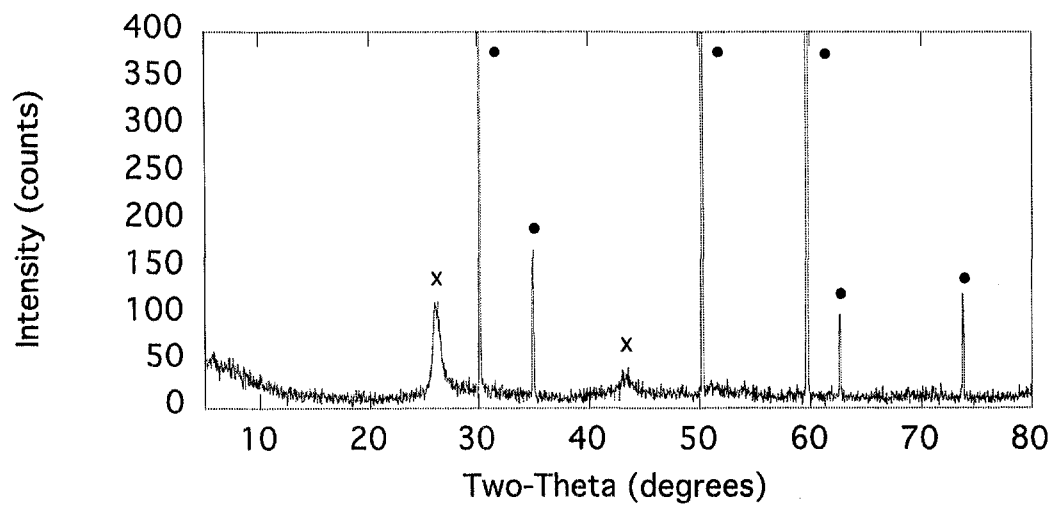


Fig 46

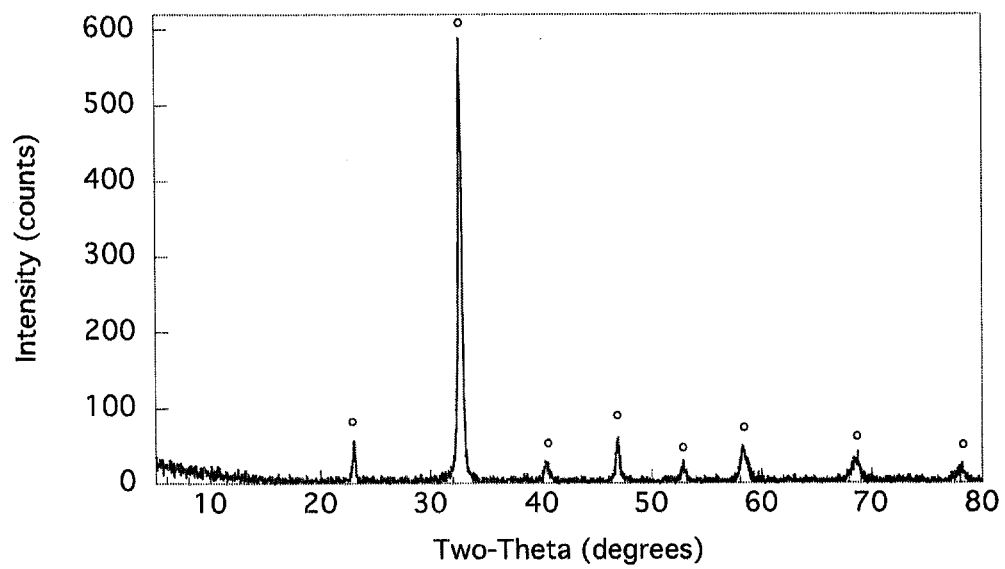


Fig 5

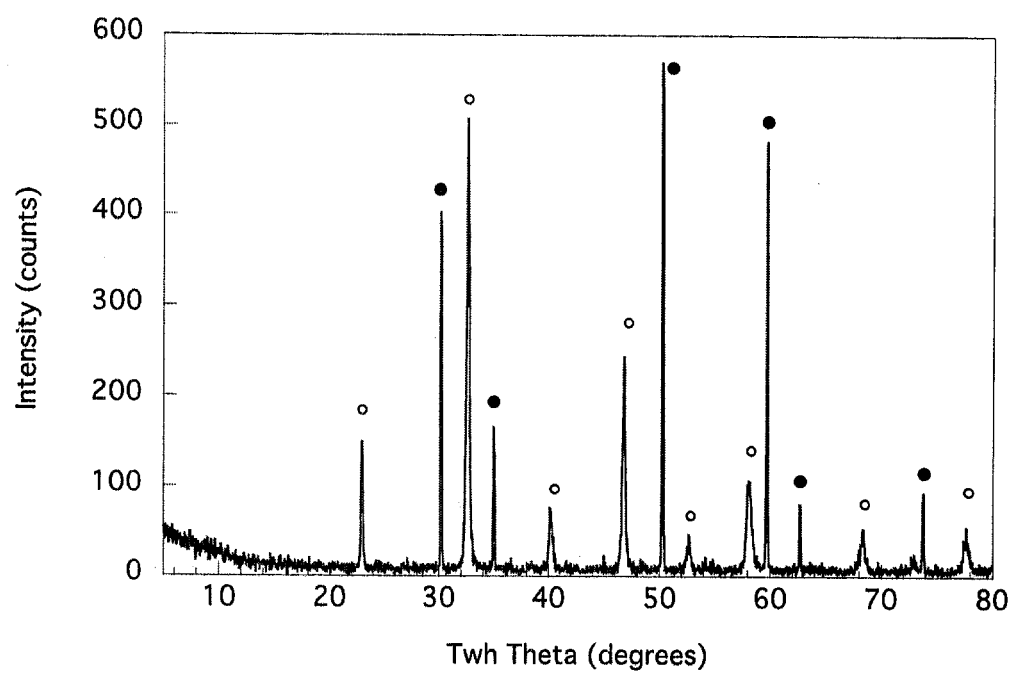


Fig 6

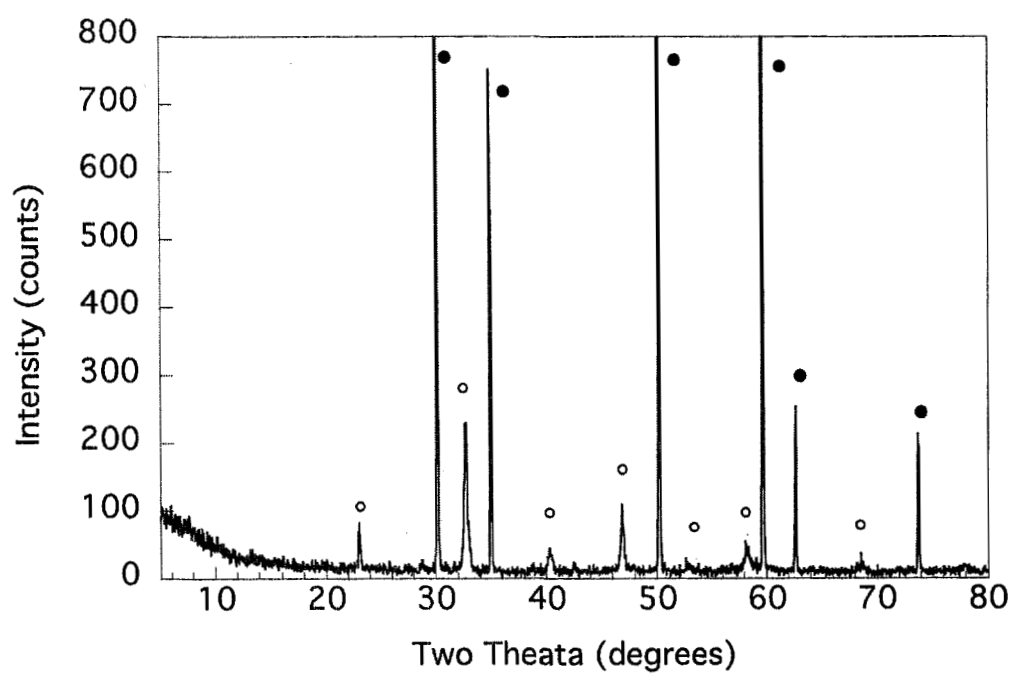


Fig 7

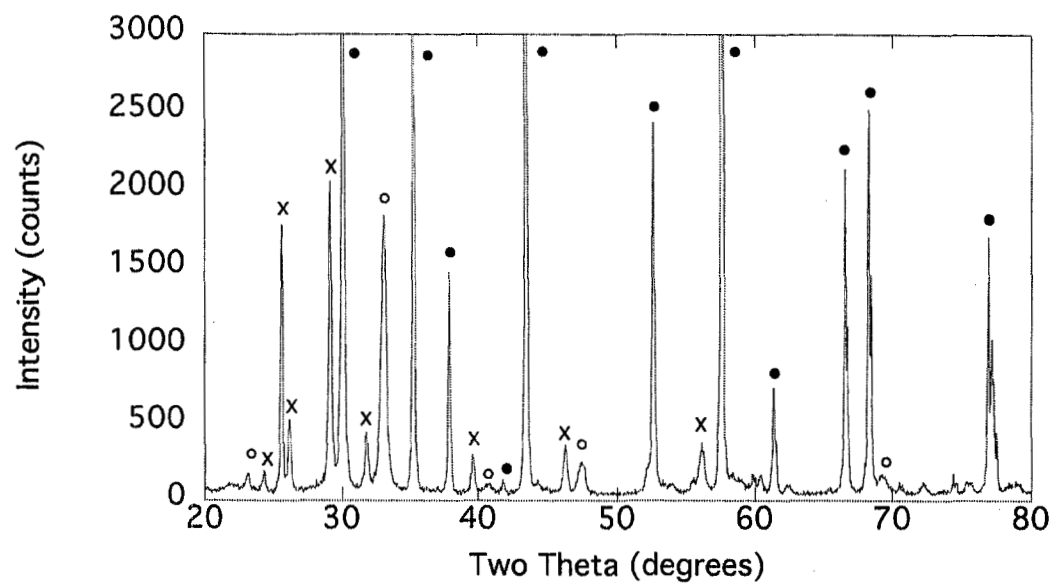


Fig 8

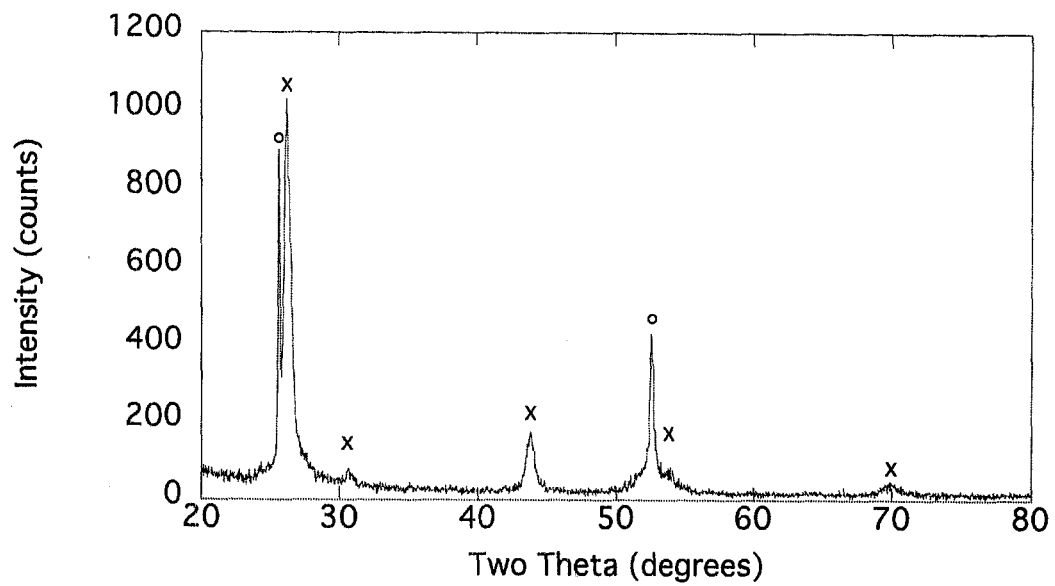


Fig 9